

3/1985

09/923709

JC03 Rec'd PCT 05 DEC 2001

SPECIFICATION

Assistant for digesting lignocellulose material and method for producing pulp

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a digestion assistant for alkaline digesting or sulfite digesting of a lignocellulose material and a method for producing pulp.

Prior Art

In the case of producing pulp by alkaline digesting or sulfite digesting of a lignocellulose material of wood or non-wood (herbage and the like), a widely known method to be employed is a method for digesting (Japanese Patent Application Laid-Open No. Sho 53-74101) by adding a small amount of hydroxyanthracene derivative to produce a high quality product economically while lowering the raw wood unit consumption and energy unit consumption. Further, in order to heighten the efficiency of a quinone type digestion assistant, known is a pulp production method (Japanese Patent Publication No. Hei 1-20276) for digesting by adding a water-soluble dihydroxyanthracene compound and a penetration accelerating agent. Further, known is a method (Japanese Patent Publication No. Sho 53-28522) comprising digesting process using an alkyl polyoxyalkylene ether carboxylic acid salt as a de-resin agent for the digesting process.

09926709-120501

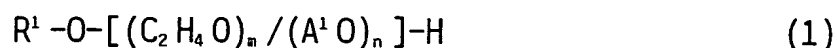
In a conventional method using a quinone type digestion assistant, the problem to be solved has been how to heighten the penetration of a quinone to the pulp. For example, even if a penetrant as disclosed in Japanese Patent Publication No. Hei 1-20276 is added, it is not satisfactory to improve the digesting yield (the yield of pulp after digesting, hereinafter the same), the digesting rate, and the quality of pulp. Further, use of a surfactant as disclosed in Japanese Patent Laid-Open No. Sho 53-28522 in the digesting process is effective for removing resin, however it has not provided sufficient effect to improve the digesting yield, the digesting rate, and the quality of pulp.

Inventors of the invention have enthusiastically made investigations aiming to improve the digesting yield, the digesting rate, and the quality of pulp in the digesting process of lignocellulose material and consequently found that use of a specified compound as a digestion assistant can improve the pulp yield after digesting, lower the Kappa number of pulp after digesting, improve the digesting rate, lower the steam energy at the time of digesting, lower the sulfidity of a digesting liquor, lower the active alkali of the digesting liquor, and further improve the tear index, the breaking length and the burst index, and improve the pulp quality.

SUMMARY OF THE INVENTION

The invention relates to an assistant for digesting a lignocellulose material and a method for producing a pulp, and a first

assistant for digesting a lignocellulose material of the invention comprises a nonionic surfactant (A) comprising one or more compounds represented by the general formula (1):

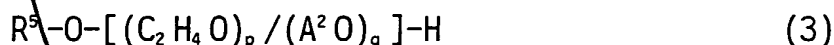


wherein R^1 is a branched alkyl group containing 4-24 carbon atoms represented by the general formula (2):



(wherein R^2 and R^3 are independently selected from the group consisting of straight-chain or branched alkyl groups containing 1-21 carbon atoms, and R^4 is an alkylene group containing 1-21 carbon atoms); m is an integer of at least 1, having an average of 4-20; A^1 is an alkylene group containing 3 or 4 carbon atoms; and n is 0 or an integer of at least 1, having an average of 0-15; wherein (C_2H_4O) and (A^1O) , in case of the average of n being 1-15, are linked random-wise and/or block-wise.

~~bbp~~ A second assistant for digesting a lignocellulose material of the invention comprises a nonionic surfactant (B) obtained by addition of an alkylene oxide to an aliphatic alcohol, said nonionic surfactant (B) comprising one or more compounds represented by the general formula (3):



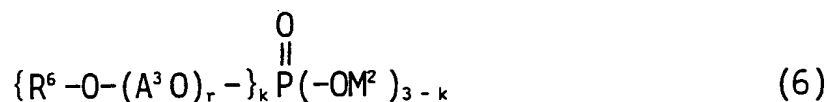
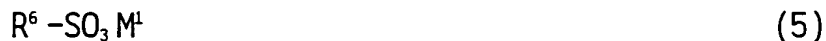
wherein R^5 is a straight-chain, branched or cyclic aliphatic hydrocarbyl group containing 4-24 carbon atoms; p is an addition molar number of 4-20; A^2 is an alkylene group containing 3 or 4 carbon atoms;

and q is an addition molar number of 0 or 1-15; wherein (C₂H₄O) and (A¹O), in case of the average of q being 1-15, are linked random-wise and/or block-wise; said nonionic surfactant (B) having a weight-average molecular weight (M_w) and a number-average molecular weight (M_n) providing a ratio of M_w/M_n satisfying the relationship (4):

$$M_w/M_n \leq -0.183 \times K^{-0.930} \times \ln X + 1.327 \times K^{-0.065} \quad (4)$$

wherein LnX is a natural logarithm of X; X is an average addition molar number of the alkylene oxide per 1 mole of the aliphatic alcohol; and K is the number of carbon atoms in R⁵ of the general formula (3).

A third assistant for digesting a lignocellulose material of the invention comprises an anionic surfactant (C) represented by the general formula (5) and/or an anionic surfactant (D) comprising one or more compounds represented by the general formula (6):



wherein R⁶ is a straight-chain, branched or cyclic aliphatic hydrocarbyl group containing 4-24 carbon atoms; A³ is an alkylene group containing 3 or 4 carbon atoms; r is 0 or an integer of at least 1, having an average of 0-15; k is an integer of 1 or 2; and M¹ and M² are monovalent cations.

A fourth assistant for digesting a lignocellulose material of the invention comprises:

(a) a nonionic surfactant (A) and/or a nonionic surfactant (B);

together with

(b) at least one anionic surfactant selected from the group consisting of an anionic surfactant (C), an anionic surfactant (D) and an anionic surfactant (E);

in a weight ratio of 100/0.1 - 100/30.

Incidentally, the surfactant (A), the surfactant (B), the surfactant (C) and the surfactant (D) are same as described, and the surfactant (E) comprises one or more compounds represented by the general formula (7):



wherein R^7 is a straight-chain or branched alkyl group, alkenyl group, or mono- or di-hydroxyalkyl group, containing 4-24 carbon atoms; R^8 is an alkylene group containing 1-6 carbon atoms; A^4 is an alkylene group containing 3 or 4 carbon atoms; s is 0 or an integer of at least 1, having an average of 0-15; and M^3 is a monovalent cation.

Further, the method for producing a pulp of the invention comprises digesting a lignocellulose material with an alkali or a sulfite in the presence of a digestion assistant; wherein the above-described assistant is used together with a quinone type digestion assistant and/or a polysulfide as the assistant.

Incidentally, the lignocellulose material is heated after, during and/or before addition of the above-described assistant in some cases.

The digestion assistant of the invention has the following characteristics by being used for alkaline digesting or sulfite

09926709-120501

digesting of a lignocellulose material:

- (1) capable of improving the digesting rate, the digesting yield and the pulp strength;
- (2) capable of further heightening the digesting accelerating effect by a quinone type digestion assistant; and
- (3) capable of suppressing the adhesion of scales in a digesting apparatus which badly affect the operation efficiency and maintenance.

Owing to the above-described effects, the digestion assistant of the invention is extremely practically useful to lower the wood unit consumption and energy unit consumption, which are important in pulp production, and to economically produce a high quality product. Further, use of the digestion assistant of the invention makes an apparatus for foam suppression and addition of a defoaming agent unnecessary and the digestion assistant can highly effectively and economically solve the above-described conventional problems.

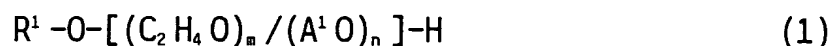
Brief Description of the Drawings

Fig. 1 shows a graph showing the range satisfying the relationship (4) or (a) in the case K is 4. Fig. 2 shows a graph showing the range satisfying the relationship (4) or (a) in the case K is 12. Fig. 3 shows a graph showing the range satisfying the relationship (4) or (a) in the case K is 24.

Best Mode for Carrying out the Invention

A first example of embodiments of the invention will be

described. The digestion assistant in this example comprises a nonionic surfactant (A) comprising one or more compounds represented by formula (1).



In the formula, R^1 is a branched alkyl represented by formula (2) and the number of carbon atoms is generally 4-24, preferably 6-20, and especially preferably 8-14. If the number of carbon atoms is less than 4 or more than 24, the surface activity is decreased and a sufficient penetration effect cannot be provided. Incidentally, in the case R^1 is, as described above, a branched alkyl group, a desirable penetration effect can be achieved.



In the formula, R^2 and R^3 are independently selected from the group consisting of straight-chain or branched alkyl groups containing 1-21 carbon atoms, and R^4 is an alkylene group containing 1-21 carbon atoms. Practical examples of R^2 and R^3 are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, isohexyl, hexyl composed of dimmers of propylene, n-heptyl, n-octyl, n-nonyl, nonyl composed of trimmers of propylene, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-eicosyl, and branched alkyl groups containing 4-21 carbon atoms synthesized by an oxo method. Practical examples of R^4 are methylene, ethylene, n-propylene, n-butylene, n-pentylene, n-hexylene, n-heptylene, n-octylene, n-nonylene,

n-decylene, n-undecylene, n-dodecylene, n-tridecylene, n-tetradecylene, n-pentadecylene, n-hexadecylene, n-heptadecylene, n-octadecylene, n-nonadecylene, n-eicosylene and the like.

Examples of the alkyl group represented by the formula (2) are isobutyl, isopentyl, isohexyl, isoheptyl, isoctyl, 2-ethylhexyl, isononyl, isodecyl, a branched nonyl composed of trimmers of propylene, isoundecyl, isododecyl, a branched dodecyl composed of tetrammers of propylene, isotridecyl, isotetradecyl, isopentadecyl, isohexadecyl, isoheptadecyl, isooctadecyl, isoeicosyl, a branched alkyl group containing 4-24 carbon atoms synthesized by an oxo method, and the like. Preferable are 2-ethylhexyl, isononyl, isodecyl, a branched nonyl composed of trimmers of propylene, isoundecyl, isododecyl, a branched dodecyl composed of tetrammers of propylene and isotridecyl. Especially preferable are 2-ethylhexyl, isononyl and isodecyl.

The above-described m of the formula (1) is generally an integer of at least 1, having an average of 4-20, preferably an integer of at least 1, having an average of 5-18 and especially preferably an integer of at least 1, having an average of 6-16. If the average of m is less than 4, the penetration effect is decreased. Contrary, if the average of m is more than 20, the penetration effect is decreased and at the same time foaming suppression becomes difficult.

A^1 of the formula (1) is an alkylene group containing of 3 or 4 carbon atoms. If the number of carbon atoms of the alkylene group is less than 3, the function of suppressing foaming becomes slight to make

it difficult to improve drainability of the black liquor in a washer. If the number of carbon atoms of the alkylene group is more than 4, the penetration function is decreased and at the same time the adsorption amount of the digestion assistant in the pulp is increased to change the surface properties of the pulp.

A^1O of the formula (1) is an oxyalkylene group formed by addition of alkylene oxide containing 3 or 4 carbon atoms. Examples of the alkylene oxide are propylene oxide (hereinafter abbreviated PO), 1,2- or 2,3-butylene oxide (hereinafter abbreviated BO), tetrahydrofuran (hereinafter abbreviated THF) and combinations of two or more of alkylene oxides containing 3 or 4 carbon atoms and preferable one is PO.

The above-described n of the formula (1) is generally 0 or an integer at least 1, having an average of 0-15, preferably 0 or an integer at least 1, having an average of 0-10 and especially preferably 0 or an integer at least 1, having an average of 0-7. If the average of n is higher than 15, the penetration effect is decreased and at the same time, the adsorption amount of the digestion assistant in the pulp is increased to change the surface properties of the pulp.

$(C_2H_4O)_m/(A^1O)_n$ of the formula (1) is a polyoxyalkylene group formed by addition of ethylene oxide (hereinafter abbreviated as EO) in m mole or (co)addition of an alkylene oxide containing 3 or 4 carbon atoms in n mole together with the EO addition, and (C_2H_4O) and (A^1O) , in case of the average n being 1-15, are linked random-wise and/or block-wise. Incidentally, the addition order is not restricted.

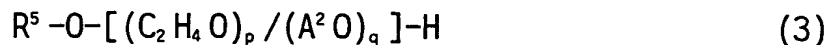
Practical examples of the nonionic surfactant (A) are those containing an alcohol represented by R^1-OH to which EO, PO and BO are added in the following order (a) to (c). Incidentally, in the following, (EO) is EO residue, (PO) is PO residue, and (BO) is BO residue, the number written at the right of each () is the number of moles of addition, // is addition in a random form, - is addition in a block form and those shown in $\langle \rangle$ show the relations between m and n in the respective compounds with α to λ .

- (a) $-(EO)_\alpha -(BO)_\beta -(EO)_\gamma -(PO)_\delta -$
 $\langle m = \{\alpha + \gamma\}, n = \{\beta + \delta\} \rangle$
- (b) $-(BO)_\varepsilon -(EO)_\zeta //(PO)_\eta -$
 $\langle m = \zeta, n = \{\varepsilon + \eta\} \rangle$
- (c) $-(EO)_\theta -(PO)_\iota -(EO)_\kappa -(PO)_\lambda -(EO)_\mu -$
 $\langle m = \{\theta + \kappa + \mu\}, n = \{\iota + \lambda\} \rangle$

Among the compounds represented by the formula (1), preferable are those composed of an alcohol represented by a formula R^1-OH and either EO added to the alcohol or EO and PO added together to the alcohol.

Next, a second example of an embodiment of the invention will be described. The digestion assistant of this example comprises a nonionic surfactant (B) obtained by addition of an alkylene oxide to an aliphatic alcohol. The nonionic surfactant (B) comprises one or more compounds represented by the formula (3) and nonionic surfactant (B) having a weight-average molecular weight (M_w) and a number-average molecular weight (M_n) providing a ratio of M_w/M_n satisfying the

relationship (4):



Incidentally, the weight-average molecular weight (M_w) can be defined as $M_w = \sum (N_i \times M_i^2) \div \sum (N_i \times M_i)$ in polydisperse system comprising molecules with molecular weight of M_i in N_i by number ($i = 1, 2, \dots$). In the equation, \sum is the summation (hereinafter the same). The number-average molecular weight (M_n) can be defined as $M_n = \sum (N_i \times M_i) \div \sum N_i$ in polydisperse system comprising molecules with molecular weight of M_i in N_i by number ($i = 1, 2, \dots$).

Further, R^5 is a straight-chain branched or cyclic aliphatic monovalent hydrocarbyl group, and the number of carbon atoms is generally 4-24, preferably 6-20 and especially preferably 8-14. If the number of carbon atoms is less than 4 or more than 24, a sufficient penetration effect cannot be obtained and that is not preferable for a digestion assistant.

Practical examples of R^5 are a straight-chain alkyl group such as n-butyl, n-pentyl, n-hexyl, n-octyl, n-nonyl, n-decyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, n-nonadecyl and the like; a branched alkyl group practically exemplified as the alkyl group in the formula (2); a cycloalkyl group such as cyclohexyl, ethylcyclohexyl, propylcyclohexyl, octylcyclohexyl, nonylcyclohexyl, adamantyl and the like; a straight-chain alkenyl or alkadienyl such as allyl, butenyl, hexenyl, octenyl, dodecenyl, tridecenyl, pentadecenyl, oleyl, gadoleyl, linoleyl and the like; a branched alkenyl or alkadienyl group such as 2-methyl-2-propenyl,

2,3-dimethyl-1,3-butadienyl, 2-ethyl-1-hexenyl, 2-ethyl-3-hexenyl, 2,6-dimethyl-7-octenyl, 2,5,8-trimethyl-3,7-nonadienyl, 2,15-dimethyl-9,10-hexadecadienyl and the like; and a cyclic alkenyl group such as 4-methyl-1-cyclopentenyl, 6-ethyl-1,3-cyclohexadienyl, 3,5-diethyl-1-cyclopentenyl, 3-(1-methylbutyl)-1-cyclohexenyl, 1-(2-propenyl)-cyclohexenyl and the like. Among them, preferable are straight-chain or branched alkyl, or alkenyl groups containing 6-20 carbon atoms and especially preferable are n-octyl, n-nonyl, n-decyl, isooctyl, 2-ethylhexyl, isononyl, and isodecyl.

The above-described p of the formula (3) is generally an integer of 4-20, preferably 5-18 and especially preferably 6-16. If p is less than 4, the penetration effect is decreased. Contrary, if p is more than 20, the penetration effect is decreased and at the same time, foaming increase.

A^2 of the formula (3) is an alkylene group containing 3 or 4 carbon atoms. If the number of carbon atoms of the alkylene group is less than 3, the foaming suppressing function becomes slight to make it difficult to improve drainability of the black liquor in a washers. On the other hand, if the number of carbon atoms of the alkylene group is more than 4, the penetration effect is decreased and at the same time, the adsorption amount of the digestion assistant in the pulp is increased to change the surface properties of the pulp. Practical examples of A^2O are same as those exemplified as the practical examples A^1O of the formula (1), and preferable is PO residue.

The above-described q of the formula (3) is generally an integer

of 0 or 1-15, preferably 0 or 1-10 and especially preferably 0 or 1-7. Those with q more than 15 are not preferable as a digestion assistant since the penetration effect is decreased.

$(C_2H_4O)_p/(A^2O)_q$ of the formula (3) is a polyoxyalkylene group formed by addition of EO in p mole or (co)addition of an alkylene oxide carbons 3 or 4 carbon atoms in q mole together with the EO addition. Practical examples of the addition type of $(C_2H_4O)_p/(A^2O)_q$ are same as described in the description for the formula (1). Incidentally, in the above-described relationship between m and n with α to λ , m is replaced by p and n is replaced by q.

Further, the nonionic surfactant (B) of the invention satisfies relationship (4).

$$Mw/Mn \leq -0.183 \times K^{-0.930} \times \ln X + 1.327 \times K^{-0.065} \quad (4)$$

The ratio Mw/Mn of the weight-average molecular weight (Mw) and the number-average molecular weight (Mn) shows the degree of the molecular weight distribution. Mw/Mn is 1 or higher and that Mw/Mn = 1, especially, means a monodispersion (composed of compounds with only a single molecular weight).

Measurement of Mw and Mn is carried out by gel permeation chromatography (GPC) using tetrahydrofuran as a developing solvent.

$\ln X$ is a natural logarithm of X; X is an average addition molar number of the alkylene oxide (including EO) per 1 mole of the aliphatic alcohol; K is the number of carbon atoms in R^5 of the formula (3).

If the Mw/Mn of the nonionic surfactant (B) satisfies the relationship (4), an excellent penetration effect can be obtained and

at the same time, foaming control is made easy. Especially preferable are those which satisfy that the value calculated by subtracting the value of Mw/Mn in the left from the value calculated in the right in the relationship (4) is 0.02 or higher. Incidentally, that the value of Mw/Mn is small means that the molecular weight distribution range is narrow and the ratio of a main component having the penetration effect is increased. Further, it is preferable that Mw/Mn satisfies relationship (a).

$$\text{Mw/Mn} \leq -0.183 \times K^{-0.930} \times \text{LnX} + 1.31 \times K^{-0.065} \quad (\text{a})$$

In the relationship, LnX, X, and K respectively are same as those of the relationship (4).

Examples of a production method of the nonionic surfactant (B) having Mw/Mn satisfying the above-described relationship (4) are as follows:

[1] a method for adding an alkylene oxide to an aliphatic alcohol using a catalyst capable of narrowing the molecular weight distribution as compared with a well known general catalyst (a basic catalyst such as hydroxides, carbonates or amine compounds of alkali metals such as lithium, sodium, potassium, cesium and the like); [2] a method comprising steps of adding 1 to 3 mole of an alkylene oxide to an aliphatic alcohol using a well-known general catalyst, removing the unreacted alcohol, and after that, adding an alkylene oxide using a well-known general catalyst; and [3] a method comprising a step of further adding an alkylene oxide using a well-known general catalyst after an alkylene oxide is added by the above-described method [1].

Preferable is the production method [1] or [3].

As a catalyst capable of narrowing the molecular weight distribution, examples are catalysts selected from a compound comprising fired magnesium oxide (Japanese Patent Application Laid-Open No. Hei 1-164437), burned hydrotalc (Japanese Patent Application Laid-Open No. Hei 2-71841), perchloric acid salt (U.S. Patent No. 4,112,231), perhalogenic acid (salt), sulfuric acid (salt), nitric acid (salt), and alcoholate of di- or tri-valent metals. Among them, preferable are perchloric acid salt and perhalogenic acid (salt) and more preferable ones are magnesium salt, zinc salt, and/or aluminum salt of perchloric acid.

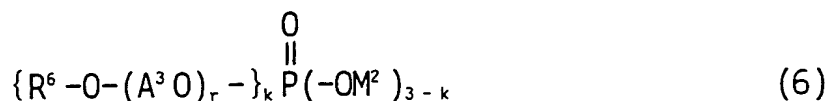
Fig. 1 to Fig. 3 show the ranges satisfying the relationship (4) or (a), and in the figures, the regions shown with oblique lines show the ranges satisfying the relationship (4) and the regions shown with cross oblique lines show the ranges satisfying the relationship (a). Additionally, the axis of abscissas of each figure shows X in the relationship (4) or (a); the axis of ordinates shows M_w/M_n . Further, Fig. 1 shows a graph showing the case K is 4 in the relationship (4) or (a); Fig. 2 shows a graph showing the case K is 12 in the relationship (4) or (a); and Fig. 3 shows a graph showing the case K is 24 in the relationship (4) or (a). Further, the results in the case of adding EO using a well-known general catalyst (potassium hydroxide) are shown with thin curved lines in the respective figures.

HLB of the nonionic surfactant (A) or the nonionic surfactant (B) of the invention is preferably 6-18, especially preferably 10-16.5.

If HLB is 6-18, a higher penetration effect can be obtained.

In this case, HLB (Hydrophile-Lipophile Balance) can be calculated by adding the numeral values showing the organic and inorganic properties (Oda, Teramura, Synthesis and Application of Surfactant, p. 501, Maki Publisher).

A third example of an embodiment of the invention will be described. The digestion assistant of this example comprises an anionic surfactant (C) represented by formula (5) and/or an anionic surfactant (D) comprising one or more compounds represented by formula (6).



In the formulas, R^6 is a straight-chain, branched or cyclic aliphatic monovalent hydrocarbyl group, and the number of carbon atoms is generally 4-24, preferably 6-20 and especially preferably 8-14. If the number of carbon atoms is less than 4 or more than 24, a sufficient penetration effect cannot be obtained and that is not preferable for a digestion assistant. Practical examples of R^6 are same as those exemplified as the practical examples of R^5 in the formula (3) and preferable one is a straight-chain or branched alkyl group, or alkenyl group containing 6-20 carbon atoms. Especially preferable one is a straight-chain or branched alkyl group containing 8-14 carbon atoms.

A^3 of the formula (6) is an alkylene group containing 2-4 carbon

atoms. If the number of carbon atoms is less than 2, it is difficult to improve the penetration effect function. Contrary, if the number of carbon atoms is more than 4, the adsorption amount of the digestion assistant in the pulp is increased to change the surface properties of the pulp. Practical examples of A^3 are ethylene, propylene, 1,2- or 2,3-butylene, tetramethylene, and combinations of these groups. Among them, preferable one is ethylene or propylene.

The above-described r of the formula (6) is generally 0 or an integer of at least 1, having an average of 0-15, preferably 0 or an integer of at least 1, having an average of 0-10 and especially preferably 0 or an integer of at least 1, having an average of 0-7. If the average of r is more than 15, the penetration effect is decreased and it is not preferable for the digestion assistant.

Usable as the anionic surfactant (D) are a monophosphate in which k is 1 in the formula (6), a diphosphate in which k is 2 and their mixture. Preferable is a monophosphate or a mixture comprising mainly a monophosphate (55% by weight or higher content). Other than mono- and/or di-phosphate, a triphosphate in which k is 3 may be produced in a small ratio (5% by weight or less) as a byproduct. Further, a condensate produced by condensation of two or more molecules of mono-, di-, and/or triphosphate may be produced as a byproduct.

M^1 of the formula (5) and M^2 of the formula (6) are monovalent cations. If M^1 and M^2 are cations with di- or higher valence, those surfactants become easy to be insoluble and the penetration function is decreased to make it difficult to increase the pulp yield. Further,

adsorption of the digestion assistant to the pulp easily takes place to change the surface properties of the pulp. As the above-described cation, examples are hydrogen ion; an alkali metal ion of such as sodium, potassium, lithium and the like; and ammonium ion, an organic ammonium ion. Among them, examples of the organic ammonium ion are quaternary ammonium ions containing 4-26 carbon atoms, e.g., tetramethylammonium ion, hexyltrimethylammonium ion, octyltrimethylammonium ion, 2-ethylhexyltrimethylammonium ion, didecyltrimethylammonium ion, trioctyltrimethylammonium ion, dilauryldimethylammonium ion, and the like; cations obtained by bonding hydrogen ion to primary, secondary or tertiary alkylamines containing 1-25 carbon atoms, e.g., cations obtained by bonding hydrogen ion to methylamine (mono-, di-, or tri-amine, hereinafter the same), ethylamine, propylamine, laurylamine, stearylamine, lauryldimethylamine and cyclohexylamine, trioctylamine, dilaurylmonomethylamine, and the like; cations obtained by bonding hydrogen ion to alkanolamine containing 2-24 carbon atoms, e.g. cations obtained by bonding hydrogen ion to ethanolamine (mono-, di-, or tri-amine, hereinafter the same), propanolamine, butanolamine, octanolamine, and the like. Among them, especially preferable are sodium ion as an alkali metal, 2-ethylhexyltrimethylammonium ion and octyltrimethylammonium ion as an organic ammonium ion, and triethanolamine cation.

In the case of $k = 1$ in the formula (6), M^2 is the similar or dissimilar cation.

09926709-120501

A fourth example of an embodiment of the invention will be described. The digestion assistant of this example comprises:

(a) a nonionic surfactant (A) and/or a nonionic surfactant (B);
and

(b) at least one anionic surfactant selected from the group consisting of an anionic surfactant (C), an anionic surfactant (D) and an anionic surfactant (E);
in combination with each other.

Incidentally, the surfactants (A) to (D) are same as those described above and the anionic surfactant (E) is one or more compounds represented by formula (7).



In the formula, R^7 is a straight-chain or branched alkyl group, alkenyl group, or mono- or di-hydroxyalkyl group, and the number of carbon atoms is generally 4-24, preferably 6-20 and especially preferably 8-14. If the number of carbon atoms is less than 4 or more than 24, a sufficient penetration effect cannot be obtained and that is not preferable for a digestion assistant. Practical examples of R^7 are straight-chain, or branched mono- or di-hydroxyalkyl groups, which may be produced by bonding hydroxyl to the terminal or the middle of carbon chains, such as monohydroxyhexyl, monohydroxyoctyl, monohydroxydecyl, monohydroxydodecyl, dihydroxydodecyl and the like, and besides them, examples further include the straight-chain or branched alkyl group and alkenyl group exemplified as the practical examples of R^5 in the formula (3). Preferable one is a straight-chain

or branched alkyl group, or hydroxyalkyl group containing 6-20 carbon atoms, and especially preferable one is a straight-chain or branched alkyl group, or monohydroxyl group containing 8-14 carbon atoms.

A^4 of the formula (7) is an alkylene group containing 2-4 carbon atoms. If the number of carbon atoms is less than 2, it is difficult to improve the penetration function. Contrary, if the number of carbon atoms is more than 4, the adsorption amount of the digestion assistant in the pulp is increased to change the surface properties of the pulp. Practical examples of A^4 are ethylene, propylene, 1,2- or 2,3-butylene, tetramethylene, and combinations of these groups. Among them, preferable one is ethylene or propylene.

The above-described s of the formula (7) is generally 0 or an integer of at least 1, having an average of 0-15, preferably 0 or an integer of at least 1, having an average of 0-10, and especially preferably 0 or an integer of at least 1, having an average of 0-7. If the average of s is more than 15, the penetration effect is decreased and it is not preferable for the digestion assistant.

R^8 of the formula (7) is a straight-chain or branched alkylene group, and the number of carbon atoms is generally 1-6, preferably 1-4 and especially preferably 1 or 2. If the number of carbon atoms is less than 1, it is chemically unstable. Contrary, if the number of carbon atoms is more than 6, the production is not easy. Incidentally, without R^8 , the anionic surfactant (E) is unstable.

Practical examples of R^8 are methylene, ethylene, 1,3-propylene, methylethylene, ethylmethylene, 1,4-butylene,

1-methyl-1,3-propylene, 1,2-dimethylethylene, 1,1-dimethylethylene, 1-ethylethylene, n-propylmethylethylene, isopropylmethylethylene, 1,5-pentylene, 2-methyl-1,4-butylene, 1,3-dimethyl-1,3-propylene, 1,1,2-trimethylethylene, 1,1-methyl-2-ethylethylene, 1,6-hexylene, 4-methyl-1,5-pentylene, 2,4-dimethyl-1,4-butylene and the like.

M° of the formula (7) is a monovalent cation. Practical examples of M° are same as those exemplified as the practical examples of M^{\dagger} in the formula (5) and among them, especially preferable are sodium ion as an alkali metal ion, 2-ethylhexyltrimethylammonium ion and n-octyltrimethylammonium ion as an organic ammonium ion, and triethanolamine cation.

The weight ratio of the nonionic surfactant (A) and/or the nonionic surfactant (B) to at least one anionic surfactant selected from the anionic surfactants (C) to (E) is 100/0.1 - 100/30, preferably (100/0.3)-(100/20) and more preferably 100/0.5 - 100/10. In the case that the weight ratio is in a range of 100/0.1 - 100/30, the penetration effect is especially heightened.

Incidentally, although each of the surfactants (A) to (E) may be used solely to obtain a good effect, combination (mixing) use of them in the above described manner can provide a significantly high penetration effect even at a high temperature with scarcely being accompanied with increase of foaming as compared with the case of using the surfactants solely. Regarding the above described single use or combination use, preferable are:

- (a) a single use of the nonionic surfactant (B);

(b) a combination use of the nonionic surfactant (A) with the anionic surfactant (C) or the anionic surfactant (E); and

(c) a combination use of the nonionic surfactant (B) with the anionic surfactant (C) or the anionic surfactant (E). Among them, especially preferable is the combination use c.

A lignocellulose material to which the digestion assistant of the invention is applied is wood (needle-leaved-tree, broad-leaved-tree), nonwood (herbage and the like) and pulp derived from them. Practical examples of the nonwood are kenaf, bagasse, bamboof and the like.

As the digesting method of the invention, applicable digesting methods are kraft method, soda method, carbonate method, polysulfide method and the like. The digester may be either continuous type or batch type. Further, the method is applicable to a conventional continuous digesting type system and besides the system, the method is also applicable to a modified kraft digesting type system (MCC), an isothermal digesting type system (ITC) or a low solid (Lo-solid) digesting system.

One example of digesting conditions by Kraft method, which is most frequently employed, will be described below.

That is: the addition amount of the active alkali (the active alkali means the total of NaOH and Na_2S) is 12-23% by weight (relative to absolutely dried chip, conversion to Na_2O); the total digesting time is 90-500 minutes; the digesting temperature is 120-175°C; the ratio of the chip and the digesting liquor is 1/2 - 1/6; the concentration of the white liquor (the alkaline solution to be use for

digesting) to be used for digesting is 80-150 g/L; and sulfidity is 20-35% by weight.

As the sulfite digesting method of the invention, usable are an alkali sulfite process, a neutral sulfite process, and bisulfite process and the like.

The addition amount of the surfactants (A) to (E) is generally 0.001-2% by weight, preferably 0.0015-1.0% by weight and especially preferably 0.002-0.5% by weight to the absolute dry weight of a lignocellulose material. If the addition amount is 0.001-2% by weight, it is economical, and the digesting yield and the digesting rate can be improved as well.

In a method for producing a pulp by alkali digesting or sulfite digesting of a lignocellulose material in the presence of the digestion assistant, as the digestion assistant, the digestion assistant of the invention may be used solely, or the digestion assistant of the invention may be used in combination with a quinone type digestion assistant and/or a polysulfide. More excellent effects in the Kappa number of pulp after digesting, the digesting yield and the pulp strength can be provided in the case of using the digestion assistant of the invention in combination with a quinone type digestion assistant and/or a polysulfide.

In the case of using the digestion assistant of the invention in combination with a quinone type digestion assistant and/or a polysulfide, a quinone type digestion assistant, a polysulfide, an alkaline digesting liquor (white liquor) and a sulfurous acid salt may

be added solely or may be added simultaneously in combination of two or more of them.

As the quinone type digestion assistant, generally, compounds included in cyclic keto compounds are used and practically, their examples are benzoquinone, naphthoquinone, anthraquinone, anthrone, phenantherenequinone and nuclear-substituted compounds of these quinone type compounds, e.g., their alkyl, alkoxy, amino, nitro, hydroxy, halogen or carboxy-derivatives, sulfonic acid salts or carboxylic acid salts.

As the quinone type digestion assistant, hydroxyquinone type compounds, which are reduced type compounds of the above-described quinone type compounds, are used and practically, examples to be selected are anthrahydroquinone, alkylanthrahydroquinone, alkoxyanthrahydroquinone, aminoanthrahydroquinone, haloanthrahydroquinone, hydroxyanthrahydroquinone, carboxyanthrahydroquinone, tautomer of the above-described anthrahydroquinone compounds and mixtures of a plurality of above-mentioned any compounds.

As the above-described tautomer, examples are 10-hydroxy-anthrone, 1- and 2-alkyl-10-hydroxy-anthrone, 1- and 2-amino-10-hydroxy-anthrone, 1- and 2-hydroxy-10-hydroxy-anthrone, 1-and 2-halo-10-hydroxy-anthrone, and mixtures of a plurality of above-mentioned any anthrone compounds.

Further, as the cyclic keto compound to be used as the quinone type digestion assistant, usable are one or more compounds selected

from 9,10-diketohydroanthracene type compounds and 9,10-dioxyhydroanthracene type compounds, which are obtained as intermediate of anthraquinone synthesis method by Diels-Alder reaction method and are stable compounds.

As the above-mentioned 9,10-diketohydroanthracene type compounds, usable are mixtures of 1,4-dihydro-9,10-diketoanthracene, 1,2,3,4-tetrahydro-9,10-diketoanthracene, 1,4,4a,9a-tetrahydro-9,10-diketoanthracene, 2-ethyl-1,4,4a,9a-tetrahydro-9,10-diketoanthracene, 2,3-dimethyl-1,4,4a,9a-tetrahydro-9,10-diketoanthracene, 1,3-dimethyl-1,4,4a,9a-tetrahydro-9,10-diketoanthracene, 1-methyl-1,2,3,4-tetrahydro-9,10-diketoanthracene, 1,2,3,4,5,8-hexahydro-9,10-diketoanthracene, 1,4,4a,5,8,8a,9a,10a-octahydro-9,10-diketoanthracene, 2,3,6,7-tetramethyl-1,4,4a,5,8,8a,9a,10a-octahydro-9,10-diketoanthracene, 1,2,3,4,5,6,7,8-octahydro-9,10-diketoanthracene and 2,6- and 2,7-diethyl-1,4,4a,5,8,8a,9a,10a-octahydro-9,10-diketoanthracene. Among them, preferable are compounds selected from unsubstituted naphthoquinone and benzoquinone and lower alkyl-substituted Diels-Alder addition product, and from the view point of effect and economical property, suitable are 1,4-dihydro-9,10-diketoanthracene, 1,4,4a,9a-tetrahydro-9,10-diketoanthracene and 1,4,4a,5,8,8a,9a,10a-octahydro-9,10-diketoanthracene.

Further, as the above-mentioned 9,10-oxyhydroanthracene type compounds, usable are 1,4-dihydro-9,10-dioxyanthracene,

1,4,5,8-tetrahydro-9,10-dioxanthracene and 1,4,5,8,8a,10a-hexahydro-9,10-dioxanthracene, and sodium and potassium salts of 1,4-dihydro-9,10-dioxanthracene are also usable.

The addition amount of the quinone type is generally 0.005-3% by weight and preferably 0.01-1% by weight to the absolute dry weight of a lignocellulose material. If the addition amount is 0.005-3% by weight, it is economical and the digesting yield and the pulp strength can be improved and the Kappa number of pulp can be lowered.

As the polysulfides, examples are those obtained by oxidizing the digesting liquor of the lignocellulose material, or mixtures of simple sulfur with caustic soda and the like. The addition amount of the polysulfides is generally 0.1-2% by weight and preferably 0.5-1.5% by weight in terms of simple sulfur to the absolute dry weight of a lignocellulose material. If the addition amount is 0.1-2% by weight, it is economical and the digesting yield and the pulp strength can be improved and the Kappa number of pulp can be lowered.

In the case of using the quinone type digestion assistant and/or the polysulfides in combination with the surfactants (A) to (E), the weight (mixing) ratio of the quinone type digestion assistant and/or the polysulfides and the surfactants (A) to (E) is generally 1/400 - 5,000/1, preferably 1/100 - 1,667/1 and especially preferably 1/50 - 1,250/1. If the weight (mixing) ratio is 1/400 - 5,000/1, the digesting yield and the pulp strength can be improved and the Kappa number of pulp can be lowered.

In a pulp production method using any of surfactants (A) to (E)

by previously adding them to the lignocellulose material before digesting, in the case that the digestion assistant of the invention is added, applicable is a method by adding the digestion assistant itself to the lignocellulose material or a method by adding an aqueous solution of the digestion assistant to the lignocellulose material. Between the methods, the method by adding the digestion assistant of the invention in form of an aqueous solution of 1-50% by weight concentration is especially preferable since the water in the lignocellulose material is scarcely increased and the digestion assistant can be evenly added to every corner of the lignocellulose material.

Further, as the addition method of the digestion assistant of the invention to the lignocellulose material, applicable is a method by spraying the digestion assistant to the lignocellulose material, a method by applying the digestion assistant to the lignocellulose material and a method by immersing the lignocellulose material in the digestion assistant, and from the view point of simplicity of facilities, the method by spraying to the lignocellulose material is preferable.

The addition timing of the digestion assistant of the invention to the lignocellulose material may be optional timing (for example, immediately before) if it is before digesting. Because the digesting liquor can penetrate the lignocellulose material by doing so when digesting start. Incidentally, if it is possible for the digestion assistant added to be washed out by the time of starting the digesting

process, it is preferable to carry out countermeasure treatment to avoid that. As one example of the countermeasure treatment, applicable is a method for storing the lignocellulose material to which the digestion assistant is added indoors or in a stock tank.

At the time (after addition, during addition, and/or before addition (incidentally, they means any timing of after addition, during addition, before addition or any two or more timing of the above-mentioned timing), hereinafter the same) of adding the surfactant (A) to (E) to the lignocellulose material, it is preferable that lignocellulose material is heated. By heating an alkali digesting liquor (white liquor), a sulfurous acid salt, a quinone type digestion assistant and a polysulfide penetrate the deep inside of the lignocellulose material.

Although the timing of the heating of the lignocellulose material may be any timing before addition, during addition, and/or after addition of the surfactants (A) to (E), it is preferable to keep 0.5 minute or longer duration contacting the heated lignocellulose material with the added surfactants (A) to (E).

As the means of heating, available are a method by bringing steam directly into contact with the lignocellulose material, a method of heating the lignocellulose material by an infrared heater and a method of heating a container containing the lignocellulose material from the outside by a heating medium. In the first mentioned method, the lignocellulose material is generally heated by bringing steam directly into contact with the material after loading the lignocellulose

material to a steaming vessel. The heating temperature is preferably 50-180°C and especially preferably 80-160°C. Keeping the temperature below 180°C is preferable since the decrease of the strength of the lignocellulose material after digesting is made difficult. The heating duration is generally 0.5-30 minutes and preferably 1-10 minutes.

At the time of adding the digestion assistant of the invention to the lignocellulose material, it is more preferable to add a quinone type digestion assistant and/or a polysulfide after the lignocellulose material is heated. It is especially preferable to add a quinone type digestion assistant and/or a polysulfide after the digestion assistant of the invention is added and then heating is carried out at 50-180°C.

The surfactants (A) to (E) can be produced by a known method as follows. For example, in the case of the nonionic surfactant (A), the surfactant can be produced by causing addition reaction of an alkylene oxide to an aliphatic alcohol at 80-200°C in the presence of a well-known catalyst.

Further in the case of the nonionic surfactant (B), the surfactant can be produced by [1] a method comprising a step of adding an alkylene oxide to an aliphatic alcohol using a catalyst capable of narrowing the molecular weight distribution; [2] a method comprising steps of adding 1 to 3 mole of an alkylene oxide to an aliphatic alcohol using a well-known general catalyst adding an alkylene oxide using a well-known general catalyst after removing the unreacted

alcohol.

Further in the case of the anionic surfactant (C), the surfactant can be produced by a method comprising steps of producing a sulfonic acid compound by reaction of SO_2 with paraffin (practically by an oxysulfonation method or by an oxychlorination method) and then neutralizing the sulfonic acid compound with a prescribed amount of at least one compound selected from an alkali metal hydroxide (e.g. sodium hydroxide, potassium hydroxide and the like), an ammonia, and an organic amine. Further in the case of the anionic surfactant (C) in which M^+ is a quaternary ammonium ion, the production method further comprises a step of exchanging salt with a methanol solution of a quaternary ammonium carbonate such as a methanol solution of triethylmethyl ammonium methyl carbonate after the above-described neutralization, and then removing methanol to obtain the surfactant.

Further in the case of the anionic surfactant (D), the surfactant can be produced by a method comprising steps of producing a phosphoric acid ester compound by reaction of a phosphoric acid compound (e.g. phosphoric acid anhydride, polyphosphoric acid, phosphorus oxychloride, and the like) with an aliphatic alcohol, and then neutralizing (salt-exchanging) the compound in the same manner as that of the anionic surfactant (C).

Further in the case of the anionic surfactant (E), the surfactant can be produced by a method comprising steps of producing a carboxylic acid compound by reaction of a monochloroalkylcarboxylic acid (e.g. monochloroacetic acid, and the like) with the nonionic surfactant (A),

the nonionic surfactant (B), or their precursor (e.g. aliphatic alcohol or its alkylene oxide adduct in a low mole ratio), and then neutralizing (salt-exchanging) the compound in the same manner as that of the anionic surfactant (C). In the case of the anionic surfactant (E) in which R^7 is mono- or di-hydroxyalkyl, the production method comprises steps of producing a carboxylic acid compound by reaction of a monochloroalkylcarboxylic acid (e.g. monochloroacetic acid, and the like) with an alkenylmonool alkylene oxide adduct, then carrying out the reaction product with diborane for borohydroxylation, and then carrying out the reaction product with hydrogen peroxide in alkaline condition (e.g. with NaOH, and the like).

Practical examples of the surfactants (A) to (E) solely or their mixtures are described as follows. Incidentally, in the following formulas, (EO) is EO residue, (PO) is PO residue, (BO) is 1,2-BO residue, (THF) is THF residue, the number written at the right side of () is the number of average moles of addition (the numeral value calculated from the mole average of the mixtures of some single molecules), // is addition in a random form and - is addition in a block form (hereinafter the same). (M_w/M_n) in { } is the value calculated from the actually measured value, $(M_w/M_n)_{cal.}$ in { } is the value of the right side of the relationship (4), and HLB is a value calculated from the numeral values showing the organic and inorganic properties.

[Practical examples of surfactant (A)]

A1: isodecyl-O-(PO)₁-(EO)₁₀-H

$\{(Mw/Mn) = 1.213, (Mw/Mn)_{cal.} = 1.091, HLB; 14.5\}$

un-reacted alcohol: 3.1% by weight

A2: isododecyl-O-[(EO)₁₀ //(PO)₁ //(BO)_{0.5}]-H

A3: isooctadecyl-O-(EO)₄-(BO)₁-(EO)₅-H

A4: 2-ethylhexyl-O-(PO)₁-(EO)₈-(PO)₁-H

A5: isobutyl-O-(PO)₁-(EO)₁₂ //(PO)₁-H

A6: isodecyl-O-[(EO)₁₈ //(PO)₃]-(PO)₇-H

A7: isobutyl-O-(EO)₇-(PO)₁-H

A8: isotetraeicosyl-O-(EO)₁₆ //(PO)₅-H

A9: isoeicosyl-O-(EO)₁₆ //(BO)_{0.1}-H

A10: 2-ethylhexyl-O-[(EO)₁₀ //(PO)₁]-H

$\{(Mw/Mn) = 1.201, (Mw/Mn)_{cal.} = 1.096, HLB; 14.5\}$

un-reacted alcohol: 3.7% by weight

A12: isodecyl-O-(EO)₁₀-H

A13: 2-ethylhexyl-O-(EO)₁₂-H

A14: 2,4-dimethylheptyl-O-[(EO)₉ //(PO)₂]-H

A15: isooctadecyl-(EO)₂₀-(THF)₁-H

A16: isotetradecyl-O-(EO)₂₀-(PO)₁₅-H

A17: isohexyl-O-[(EO)₄ //(PO)_{0.1}]-H

A18: isoeicosyl-O-(EO)₂₀-(PO)₁₀-H

[Practical examples of surfactant (B)]

B1: n-octyl-O-[(EO)₁₀ //(PO)₁]-H

$\{(Mw/Mn) = 1.056, (Mw/Mn)_{cal.} = 1.096, HLB; 14.3\}$

un-reacted alcohol: 0.5% by weight

B2: 2-ethylhexyl-O-[(EO)₁₀ //(PO)₁]-H

$\{(Mw/Mn) = 1.053, (Mw/Mn)_{cal.} = 1.096, HLB; 14.5\}$

un-reacted alcohol: 0.4% by weight

B3: n-octyl-O-[(EO)₁₀/(PO)₂]-H

$\{(Mw/Mn) = 1.043, (Mw/Mn)_{cal.} = 1.093\}$

B4: n-trideca-2-enyl-O-(EO)₁₅-(PO)₇-H

$\{(Mw/Mn) = 1.037, (Mw/Mn)_{cal.} = 1.071\}$

B5: isodecyl-O-(PO)₃-(EO)₁₈-(PO)₄-H

$\{(Mw/Mn) = 1.039, (Mw/Mn)_{cal.} = 1.073\}$

B6: n-octadeca-2-enyl-O-(EO)₁₅-H

$\{(Mw/Mn) = 1.041, (Mw/Mn)_{cal.} = 1.066, HLB; 14.8\}$

un-reacted alcohol: 0.7% by weight

B7: 4-ethylcyclohexyl-O-(EO)₁₂-H

$\{(Mw/Mn) = 1.039, (Mw/Mn)_{cal.} = 1.093, HLB; 15.9\}$

un-reacted alcohol: 0.6% by weight

B8: n-hexyl-O-(EO)₈-H

$\{(Mw/Mn) = 1.041, (Mw/Mn)_{cal.} = 1.109\}$

B9: 4-ethylcyclohexyl-O-(EO)₁₆-H

$\{(Mw/Mn) = 1.036, (Mw/Mn)_{cal.} = 1.086\}$

B10: 2-ethylhexyl-O-(EO)₁₀-H

$\{(Mw/Mn) = 1.038, (Mw/Mn)_{cal.} = 1.098\}$

© Production method of B1 to B10

An intermediate was obtained by adding 0.0003 mole of aluminum perchlorate hydrated with 9 H₂O to 1 mole of an aliphatic alcohol, and carrying out addition reaction with 2.5 mole of EO or PO in the case of homogenous or block adduct, and 2.5 mole in total of EO and PO in

the mole ratio shown in the respective chemical formulas in the case of a random adduct at 100°C. Further, the intermediate was mixed with sodium hydroxide in a proper amount equivalent to be 0.07% by weight in the final product, and EO or PO was added at 110°C solely or in a block or random form.

[Practical examples of surfactant (C)]

C1: n-tetradecyl-SO₃ Na

C2: n-decyl-SO₃ H · N(C₂ H₅ OH)₃

C3: isotetradecyl-SO₃ Na

C4: isohexyl-SO₃ H · N(C₂ H₅ OH)₃

C5: isoeicosyl-SO₃ H · NH₂ C₁₂ H₂₅

[Practical examples of surfactant (D)]

D1: n-octyl-O-PO₃ H · N(CH₃)₃ C₈ H₁₇

{monoalkylphosphate content: 84.5%}

D2: isooctyl-O-PO₃ H · N(CH₃)₃ C₈ H₁₇

{monoalkylphosphate content: 85.3%}

D3: isododecyl-O-PO₃ (Na)₂

{monoalkylphosphate content: 84.2%}

[Practical examples of surfactant (E)]

E1: isododecyl-O-(EO)₃-CH₂ COONa

E2: 2-ethylhexyl-O-C₃ H₆ COOK

E3: 2-hydroxydodecyl-O-CH₂ COONa

E4: 2-ethylhexyl-O-CH₂ COO · N(CH₃)₃ C₈ H₁₇

E5: n-dodecyl-O-(EO)₃-CH₂ COONa

[Practical Examples of Combinations (Mixtures) of Surfactant (A) to

(E)]

AC1: using A1 and C1 in 100/1 weight ratio in combination

BE2: using B1 and E3 in 100/20 weight ratio in combination

AE3: using A1 and E3 in 100/10 weight ratio in combination

AD4: using A1 and D1 in 100/0.1 weight ratio in combination

AC5: using A10 and C1 in 100/0.3 weight ratio in combination

BC6: using B2 and C1 in 100/0.5 weight ratio in combination

[Example]

Hereinafter, the invention will be described more particularly according to the examples and the comparative examples, however the invention is not at all restricted to these examples. Incidentally, the above-described A1, B2, B6, B7, C1, C2, D1, AC1 (combination (mixture) of A1 and C1), BE2 (combination (mixture) of B1 and E3), and AE3 (combination (mixture) of A1 and E3) were used for the examples and the following X1 to X6 were used for comparative examples.

X1: n-octyl-O-[(EO)₁₀/(PO)₁]-H

{(Mw/Mn) = 1.204, (Mw/Mn)_{cal.} = 1.096, HLB; 14.3}

un-reacted alcohol: 0.9% by weight

X2: 2,4,6-triethyl-eicosyl-O-(EO)₂₀-H

{(Mw/Mn) = 1.024, (Mw/Mn)_{cal.} = 1.047, HLB; 12.4}

un-reacted alcohol: 0.3% by weight

X3: isopropyl-O-(PO)₁-(EO)₆-(PO)₁-H

{(Mw/Mn) = 1.047, (Mw/Mn)_{cal.} = 1.099, HLB; 15.1}

un-reacted alcohol: 0.6% by weight

X4: iso-octadecyl-O-[(EO)₂₂/(PO)₁₆]-H

{(Mw/Mn) = 1.022, (Mw/Mn)_{cal.} = 1.054, HLB; 10.2}

un-reacted alcohol: 0.3% by weight

X5: n-propyl-SO₃Na

X6: X1 and X5 in 100/10 ratio in combination

X7: n-octylphenyl-O-(EO)₁₀-H

© Production method of X1

Sodium hydroxide in a proper amount equivalent to be 0.07% by weight in the final product was added to n-octylalcohol and a mixture of EO and PO in 10/1 mole ratio was added at 110°C for addition reaction.

© Production method of X2 to X4

An intermediate was obtained by adding 0.0003 mole of aluminum perchlorate hydrated with 9 H₂O to 1 mole of an aliphatic alcohol, and carrying out addition reaction with 2.5 mole of EO in the case of X2, 1 mole of PO and 1.5 mole of EO added in this order in the case of X3, and 2.5 mole in total of a mixture of EO and PO in 22/16 mole ratio in the case of X4 at 100°C. Further, the intermediate was mixed with sodium hydroxide in a proper amount equivalent to be 0.07% by weight in the final product, and EO or PO was added at 110°C solely or in a block or random form.

The following are description of a pulp production method after digesting (for test) carried out in the examples 1 to 71 and comparative examples 1 to 62, measurement methods for the Kappa number of pulp after digesting, the digesting yield, the tear index, the breaking length, the burst index and the foaming (foaming height), and

the measurement methods of the digesting steam quantity and the scale deposition amount.

<Pulp Production Method after digesting (for test)>

After digested pulp was put in a cloth bag and sufficiently washed with tap water, and knots were removed by a flat screen (manufactured by Kumagai Riki Kogyo Co.), and then the resulting pulp was sucked and filtered by Nutsche and formed into a sheet-like shape. This pulp is defined as pulp after digesting. Further, the obtained pulp was processed to produce a hand-made sheet (which was employed as a pulp for a paper quality test) according to the method described in JIS P 8209 after preparing the pulp at 450 mL according to Canada standard freeness described in JIS P 8121 by PFI mill described in JIS 8210.

<Measurement Method of Kappa Number of Pulp After Digesting>

The Kappa number of pulp after digesting was measured by a method described in JIS P 8211.

<Measurement Method of Digesting Yield>

The digesting yield was calculated by measuring the absolutely dried weight of pulp before digesting and the absolutely dried weight of pulp after digesting, and dividing the latter with the former as to show the yield in % by weight.

<Measurement Method of Tear Index>

The tear index was measured by the method described in JIS P 8116 using the pulp for the paper quality test.

<Measurement Method of Breaking Length>

The breaking length was measured by the method described in JIS

09869103

098607

098607

098607

09869103

[illegible]

098607

098607

09869103

to a ceramic crucible whose weight was known and heated by a gas burner to be evaporated and dried. The weight after the evaporation and drying was measured, and the weight was subtracted by the weight of the empty crucible to obtain the value defined as the scale deposition amount.

<Examples 1 to 17, Comparative examples 1 to 12>

30 g of hardwood chip was loaded to an autoclave with 200 mL capacity, and a Kraft digesting liquor with 15% of active alkali and 30% of sulfidity, which produced from NaOH and Na₂S reagents, was added in liquor ratio of 4, and then each of the digestion assistants (A1, B2, B6, B7, C1, C2, D1, AC1, BE2 and AE3) of the invention or the digestion assistants (X1 to X6) of the comparative examples and/or 1,4-dihydro-9,10-dihydroxyanthracene was added in the addition amount shown in the following Table 1, and digesting was carried out at 160 °C for 2 hours. The evaluation results are shown in Table 1.

Table 1

Test No.	Digestion assistant		Quino- ne addi- tion amount * *	Kappa number of pulp after diges- ting	Diges- ting yield (%)	Tear index	Break- ing length (km)	Burst index	Foami- ng (mm)	Scale deposit- ion amount (mg)
	Assis- tant compo- und	Addi- tion amount *								
Example										
1	A 1	0.01	0	19.9	47.3	108	5.6	4.4	26	0.10
2	A 1	0.001	0	20.2	46.9	104	5.3	4.2	25	0.17
3	A 1	0.01	0.05	19.2	48.8	119	6.4	5.2	26	0.21
4	A 1	1.00	0	19.4	47.4	108	5.6	4.6	28	0.12
5	A 1	1.00	0.05	18.0	49.3	118	6.6	5.3	28	0.20
6	B 2	0.01	0	19.7	47.5	109	5.7	4.4	26	0.11
7	B 6	0.01	0	19.8	47.3	108	5.7	4.4	25	0.12
8	B 7	0.01	0	19.5	47.7	110	5.8	4.3	26	0.11
9	C 1	1.00	0	19.9	47.1	106	5.6	4.4	47	0.07
1 0	C 1	0.01	0	19.8	47.3	108	5.6	4.4	26	0.12
1 1	C 2	0.01	0	19.9	47.3	107	5.6	4.3	26	0.11
1 2	D 1	0.01	0	19.9	47.3	108	5.6	4.4	28	0.10
1 3	AC 1	0.01	0	19.2	47.7	109	5.7	4.6	26	0.10
1 4	AC 1	1.00	0	18.7	47.9	111	5.9	4.8	28	0.06
1 5	AC 1	0.01	0.05	18.0	49.1	119	6.5	5.3	26	0.19
1 6	BE 2	0.01	0	19.2	47.6	107	5.8	4.8	26	0.11
1 7	AE 3	0.01	0	19.3	47.7	109	5.8	4.7	26	0.12
Comparative Example										
1	X 1	0.01	0	21.7	46.3	104	5.3	3.7	26	1.30
2	X 1	0.01	0.05	20.2	47.6	114	6.2	4.2	25	2.73
3	X 1	1.00	0	21.4	46.7	105	5.3	3.6	28	1.02
4	X 1	1.00	0.05	20.1	47.7	115	6.4	4.3	28	2.21
5	X 2	0.01	0	21.8	46.4	104	5.3	3.7	26	1.24
6	X 3	0.01	0	21.7	46.3	105	5.3	3.7	25	1.35
7	X 4	0.01	0	21.8	46.3	105	5.4	3.8	26	1.27
8	X 5	0.01	0	21.7	46.4	104	5.4	3.7	26	1.25
9	E 5	0.01	0	21.8	46.3	105	5.3	3.7	27	1.19
1 0	X 6	0.01	0	21.8	46.4	105	5.3	3.7	26	1.32
1 1	—	0	0	22.3	46.0	103	5.2	3.5	25	1.95
1 2	—	0	0.05	20.3	47.5	112	6.1	4.2	25	3.32

*: % by weight to the absolutely dried chip weight

* *: % by weight to the absolutely dried chip weight (using 1,4-dihydro-9,10-dihydroxy-anthracene)

<Examples 18 to 34, Comparative examples 13 to 24>

30 g of softwood chip was loaded to an autoclave with 200 mL capacity, and a soda digesting liquor to be equivalent to 19% of NaOH to absolutely dried chip was added in liquor ratio of 5, and then each of the digestion assistants (A1, B2, B6, B7, C1, C2, D1, AC1, BE2 and AE3) of the invention or the digestion assistants (X1 to X6) of the comparative examples and/or 9,10-dihydroxyanthracene was added in the addition amount shown in the following Table 2 and digesting was carried out at 165°C for 2 hours. The evaluation results are shown in Table 2.

Table 2

Test No.	Digestion assistant		Quino- ne addi- tion amount * *	Kappa number of pulp after diges- ting	Diges- ting yield (%)	Tear index	Break- ing length (km)	Burst index	Foami- ng (mm)	Scale deposit- ion amount (mg)
	Assis- tant compo- und	Addi- tion amount *								
Example										
1 8	A 1	0.01	0	37.4	48.2	174	7.7	7.0	35	0.15
1 9	A 1	0.001	0	37.6	48.1	173	7.6	7.0	34	0.17
2 0	A 1	0.01	0.05	35.7	50.1	177	9.2	7.5	35	0.26
2 1	A 1	1.00	0	37.0	48.6	174	7.6	7.1	37	0.09
2 2	A 1	1.00	0.05	35.1	50.1	178	9.3	7.5	37	0.21
2 3	B 2	0.01	0	37.4	48.4	174	7.8	7.2	35	0.14
2 4	B 6	0.01	0	37.4	48.2	175	7.8	7.2	35	0.13
2 5	B 7	0.01	0	37.4	48.5	176	7.9	7.3	34	0.13
2 6	C 1	1.00	0	37.0	48.6	174	7.7	7.1	55	0.08
2 7	C 1	0.01	0	37.4	48.2	174	7.7	7.3	34	0.14
2 8	C 2	0.01	0	37.4	48.2	174	7.7	7.2	34	0.15
2 9	D 1	0.01	0	37.4	48.1	174	7.7	7.2	34	0.14
3 0	AC 1	0.01	0	37.0	48.7	175	7.7	7.2	34	0.14
3 1	AC 1	1.00	0	36.7	49.3	178	8.3	7.2	37	0.09
3 2	AC 1	0.01	0.05	35.1	50.6	179	9.1	7.6	34	0.19
3 3	BE 2	0.01	0	37.1	48.6	176	7.8	7.3	34	0.15
3 4	AE 3	0.01	0	37.0	48.7	176	7.7	7.2	34	0.14
Comparative Example										
1 3	X 1	0.01	0	38.3	47.3	172	7.5	6.9	35	1.75
1 4	X 1	0.01	0.05	36.6	48.5	176	8.4	7.2	34	3.10
1 5	X 1	1.00	0	38.2	47.4	172	7.6	6.9	37	1.61
1 6	X 1	1.00	0.05	36.3	48.6	176	8.4	7.2	37	2.97
1 7	X 2	0.01	0	38.3	47.3	172	7.5	7.0	34	1.72
1 8	X 3	0.01	0	38.4	47.3	172	7.6	6.9	34	1.77
1 9	X 4	0.01	0	38.3	47.4	172	7.6	6.9	35	1.74
2 0	X 5	0.01	0	38.3	47.3	173	7.5	7.0	35	1.75
2 1	E 5	0.01	0	38.4	47.4	172	7.6	6.9	35	1.73
2 2	X 6	0.01	0	38.5	47.4	172	7.5	6.9	35	1.74
2 3	—	0	0	38.6	47.1	172	7.4	6.5	33	2.54
2 4	—	0	0.05	36.5	48.4	176	8.4	7.1	33	3.92

*: % by weight to the absolutely dried chip weight

* *: % by weight to the absolutely dried chip weight (using 9,10-dihydroxyanthracene)

<Examples 35 to 51, Comparative examples 25 to 36>

20 g of flax was loaded to an autoclave with 200 mL capacity, and a digesting liquor containing 17% of Na_2SO_3 and 3.5% of NaOH was added, and then each of the digestion assistants (A1, B2, B6, B7, C1, C2, D1, AC1, BE2 and AE3) of the invention or the digestion assistants (X1 to X6) of the comparative examples and/or 9,10-anthraquinone was added in the addition amount shown in the following Table 3, and digesting was carried out at 170°C for 4.5 hours. The evaluation results are shown in Table 3.

0926709.120501

Table 3

Test No.	Digestion assistant		Quino- ne addit- ion amount * *	Kappa number of pulp after Digesti- ng	Diges- ting yield (%)	Tear index	Break- ing length (km)	Foami- ng (mm)	Scale deposit- ion amount (mg)
	Assis- tant compo- und	Addit- ion amount *							
Example									
3 5	A 1	0.01	0	10.4	57.6	171	7.6	20	0.12
3 6	A 1	0.001	0	10.6	57.4	170	7.6	19	0.14
3 7	A 1	0.01	0.05	8.1	59.7	187	8.9	19	0.21
3 8	A 1	1.00	0	9.6	58.3	173	8.0	22	0.07
3 9	A 1	1.00	0.05	8.1	59.8	186	8.8	22	0.18
4 0	B 2	0.01	0	10.2	57.9	172	7.8	20	0.11
4 1	B 6	0.01	0	10.3	57.8	171	7.8	19	0.11
4 2	B 7	0.01	0	10.0	58.2	175	8.1	20	0.12
4 3	C 1	1.00	0	9.6	58.5	180	8.1	32	0.06
4 4	C 1	0.01	0	10.3	57.7	172	7.9	19	0.13
4 5	C 2	0.01	0	10.3	57.7	171	7.8	20	0.12
4 6	D 1	0.01	0	10.4	57.8	171	7.8	20	0.12
4 7	AC 1	0.01	0	9.9	58.1	176	7.8	19	0.12
4 8	AC 1	1.00	0	9.5	58.6	180	8.2	22	0.08
4 9	AC 1	0.01	0.05	8.1	59.8	187	8.8	20	0.20
5 0	BE 2	0.01	0	10.0	58.2	176	7.9	20	0.12
5 1	AE 3	0.01	0	9.9	58.1	176	7.9	20	0.13
Comparative Example									
2 5	X 1	0.01	0	11.2	57.0	168	7.2	19	1.41
2 6	X 1	0.01	0.05	8.7	58.3	174	8.5	20	2.67
2 7	X 1	1.00	0	11.0	57.2	168	7.1	22	1.16
2 8	X 1	1.00	0.05	8.6	58.4	175	8.6	22	2.43
2 9	X 2	0.01	0	11.1	57.0	166	7.2	19	1.37
3 0	X 3	0.01	0	11.2	57.0	167	7.1	19	1.45
3 1	X 4	0.01	0	11.2	57.1	166	7.1	20	1.44
3 2	X 5	0.01	0	11.2	57.0	167	7.2	19	1.47
3 3	E 5	0.01	0	11.2	57.0	166	7.1	21	1.45
3 4	X 6	0.01	0	11.1	57.0	165	7.1	20	1.46
3 5	—	0	0	11.5	56.7	165	6.8	18	1.85
3 6	—	0	0.05	8.8	58.2	173	8.4	18	3.13

*: % by weight to the absolutely dried chip weight

** : % by weight to the absolutely dried chip weight (using 9,10-anthraquione)

0926709-120501
FO502T 60292660
<Examples 52 to 59, Comparative examples 37 to 44>

30 g of softwood chip was loaded to an autoclave with 200 mL capacity and a Kraft digesting liquor with 15% of active alkali and 30% of sulfidity, which is produced from NaOH and Na₂S reagents, was added in liquor ratio of 5, and then each of the digestion assistants (A1, AC1) of the invention or the digestion assistant (X1) of the comparative examples together with 1,4-dihydro-9,10-dihydroxyanthracene and/or polysulfide produced by dissolving powdered sulfur in a caustic soda solution was added in the addition amount shown in the following Table 4, and digesting was carried out at 160°C for 2 hours. The evaluation results are shown in Table 4.

Table 4

Test No.	Digestion assistant		Quino- ne addition amount * *	Polys- ulfide addition amount * * *	Kappa number of pulp after digesti- ng	Diges- ting yield (%)	Tear index	Break- ing length (km)	Foami- ng (mm)	Scale depos- ition amount (mg)
	Assis- tant compo- und	Addit- ion amount *								
Example										
5 2	A 1	0.01	0	0	33.3	49.1	176	7.9	35	0.16
5 3	A 1	0.01	0.05	0	31.4	51.0	180	9.3	36	0.27
5 4	A 1	0.01	0.05	0.5	31.1	52.1	183	9.5	35	0.27
5 5	A 1	0.01	0	0.5	32.8	50.8	179	9.2	35	0.15
5 6	A C 1	0.01	0	0	32.8	49.6	178	8.1	35	0.14
5 7	A C 1	0.01	0.05	0	30.7	51.5	183	9.5	35	0.26
5 8	A C 1	0.01	0.05	0.5	30.5	52.8	185	9.8	34	0.27
5 9	A C 1	0.01	0	0.5	32.2	51.3	182	9.4	35	0.14
Comparative Example										
3 7	X 1	0.01	0	0	34.4	48.1	174	7.6	35	1.72
3 8	X 1	0.01	0.05	0	32.7	49.4	177	8.6	35	3.13
3 9	X 1	0.01	0.05	0.5	32.3	50.2	179	8.8	36	3.15
4 0	X 1	0.01	0	0.5	33.9	49.2	178	8.6	35	1.71
4 1	—	0	0	0	34.5	48.1	174	7.6	34	2.56
4 2	—	0	0.05	0	32.8	49.3	177	8.6	35	3.82
4 3	—	0	0.05	0.5	32.4	50.1	179	8.7	35	3.91
4 4	—	0	0	0.5	34.0	49.0	177	8.6	35	2.61

*: % by weight to the absolutely dried chip weight

**: % by weight to the absolutely dried chip weight (using 1,4-dihydro-9,10-dihydroxy-anthracene)

***: % by weight to the absolutely dried chip weight (as simple sulfur)

09026709-120501

<Examples 60 to 67, Comparative examples 45 to 58>

30 g of hardwood chip was loaded to an autoclave with 200 mL capacity and a Kraft digesting liquor produced from NaOH and Na₂S reagents was added in liquor ratio of 4, and then the digestion assistant (A1) of the invention or the digestion assistant (X1) of the comparative examples together with 1,4-dihydro-9,10-dihydroxyanthracene and/or polysulfide produced by dissolving powdered sulfur in a caustic soda solution was added in the addition amount shown in the following Table 5, and digesting was carried out at 160°C for 2 hours. The evaluation results are shown in Table 5.

Incidentally, in the examples and comparative examples (except comparative example 52), the digesting conditions for the test (the active alkali, the sulfidity, the digesting temperature, the digesting time) were adjusted so as to keep the Kapper number of them be same as the Kapper number 22.3 of the comparative example 52 (the digesting conditions: no digestion assistant addition, the active alkali: 15%, the sulfidity: 30%, the digesting temperature: 160°C, the digesting time: 2 hours). These digesting conditions are shown in Table 5.

Table 5

Test No.	Digestion assistant		Quino- ne addi- tion amount ***	Polys- ulfide addi- tion amount ***	Active alkali (%)	Sulfi- dity (%)	Digesti- ng tempera- ture (°C)	Digesti- ng time (hr)	Diges- ting yield (%)	Tear index	Break- ing length (km)	Burst index	Foami- ng (mm)	Scale deposi- tion amount (mg)	Digesti- ng steam quantity ***
	Assis- tant compo- und	Addi- tion amount *													
Example															
60	A1	0.01	0	0	15	27	160	2	46.2	105	5.3	3.6	26	0.10	100
61	A1	0.01	0	0	13.4	30	160	2	46.2	105	5.4	3.6	26	0.11	100
62	A1	0.01	0.05	0	15	14.7	160	2	46.3	106	5.3	3.7	26	0.21	100
63	A1	0.01	0.05	0	15	30	160	1.5	46.4	105	5.4	3.7	26	0.20	75
64	A1	0.01	0.05	0.5	11.1	30	160	1.5	46.5	106	5.5	3.8	25	0.22	75
65	A1	0.01	0.05	0.5	15	14.7	135	2	46.5	107	5.5	3.9	26	0.21	84
66	A1	0.01	0	0.5	15	30	138	2	46.3	105	5.3	3.8	25	0.11	86
67	A1	0.01	0	0.5	11.1	30	160	2	46.3	105	5.3	3.7	25	0.12	100
Comparative Example															
45	X1	0.01	0	0	15	29.5	160	2	46.0	104	5.2	3.5	26	1.33	100
46	X1	0.01	0.05	0	15	18	160	2	46.1	105	5.3	3.6	26	2.83	100
47	X1	0.01	0.05	0	15	30	160	1.8	46.1	105	5.2	3.6	26	2.76	91
48	X1	0.01	0.05	0.5	12.6	30	160	1.8	46.2	105	5.3	3.7	26	2.85	90
49	X1	0.01	0.05	0.5	15	18	153	2	46.3	106	5.3	3.7	25	2.81	94
50	X1	0.01	0	0.5	15	30	156	2	46.1	104	5.3	3.6	25	1.28	96
51	X1	0.01	0	0.5	14.1	30	160	2	46.1	104	5.2	3.6	25	1.28	100
52	—	0	0	0	15	30	160	2	46.0	103	5.2	3.5	25	1.96	100
53	—	0	0.05	0	15	18	160	2	46.1	104	5.2	3.6	25	3.31	100
54	—	0	0.05	0	15	30	160	1.8	46.1	104	5.2	3.6	26	3.37	91
55	—	0	0.05	0.5	12.8	30	160	1.8	46.2	104	5.3	3.6	26	3.39	91
56	—	0	0.05	0.5	15	18	155	2	46.2	105	5.3	3.6	25	3.38	96
57	—	0	0	0.5	15	30	157	2	46.1	104	5.2	3.6	25	2.09	97
58	—	0	0	0.5	14.3	30	160	2	46.1	103	5.2	3.6	26	2.02	100

※The Kappan number was 22.3 for pulp after digesting for all of the examples 61 to 68 and comparative examples 45 to 58.

*: % by weight to the absolutely dried chip weight

**: % by weight to the absolutely dried chip weight (using 1,4-dihydro-9,10-dihydroxyanthracene)

***: % by weight to the absolutely dried chip weight (as simple sulfur)

****: Shown as the index while determining the value in the case of using no digestion assistant (comparative example 52) to be 100.

<Examples 68 to 71, Comparative examples 59 to 62>

In the case of heating (steaming) after addition of the digestion assistant (A1) of the invention or the digestion assistant (X1) of the comparative example:

30 g of softwood chip was loaded to an autoclave with 200 mL capacity and a Kraft digesting liquor with 15% of active alkali and 30% of sulfidity, which is produced from NaOH and Na₂S reagents, was added in liquor ratio of 5, and then the digestion assistant (A1) of the invention or the digestion assistant (X1) of the comparative examples was added, and steaming was carried out at 100°C for 5 minutes. After that, 1,4-dihydro-9,10-dihydroxyanthracene and/or polysulfide produced by dissolving powdered sulfur in a caustic soda solution was added in the addition amount shown in the following Table 6, and digesting was carried out at 160°C for 2 hours. The evaluation results are shown in Table 6.

As compared with the results of Table 4, the digestion assistants of the invention were found more effective by being added after heating.

Table 6

Test No.	Digestion assistant		Steaming time (min)	Quino- ne addi- tion amount * *	Polysul- fide addition amount	Kappa number of pulp after diges- ting	Diges- ting yield (%)	Tear index	Break- ing length (km)	Foami- ng (mm)	Scale depos- ition amount (mg)
	Assis- tant compo- und	Addit- ion amount *									
Example											
6 8	A 1	0.01	5	0	0	32.6	49.9	179	8.1	35	0.09
6 9	A 1	0.01	5	0.05	0	30.7	51.9	183	9.6	36	0.19
7 0	A 1	0.01	5	0.05	0.5	30.3	53.2	185	9.7	35	0.19
7 1	A 1	0.01	5	0	0.5	32.1	51.8	182	9.4	35	0.09
Comparative Example											
5 9	X 1	0.01	5	0	0	34.3	48.2	174	7.7	35	1.72
6 0	X 1	0.01	5	0.05	0	32.5	49.5	177	8.6	35	3.12
6 1	X 1	0.01	5	0.05	0.5	32.4	50.3	179	8.9	36	3.14
6 2	X 1	0.01	5	0	0.5	33.9	49.3	179	8.6	35	1.70

*: % by weight to the absolutely dried chip weight

* *: % by weight to the absolutely dried chip weight (using 1,4-dihydro-9,10-dihydroxyanthracene)

* * *: % by weight to the absolutely dried chip weight (as simple sulfur)

Industrial Applicability

As described above, the assistant for digesting a lignocellulose material of the invention is useful as a digestion assistant for alkali digesting or sulfite digesting of a lignocellulose material. Further, the method for producing a pulp of the invention is useful for a method for producing pulp by alkali digesting or sulfite digesting of a lignocellulose material in the presence of the digestion assistant.